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A Note on the Specific Heat of the Hydrogen Molecule.

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In a recent article F. Hund* has treated the problem of the specific heat of the hydrogen molecule on the basis of the wave mechanics. The total number of rotational states are divided due to homopolar character of the molecule into two groups, to the one of which belong wave functions symmetrical in the two nuclei, and to the other wave functions which are antisymmetrical in the nuclei. Hund has suggested that the presence of both groups in hydrogen may be accounted for by assuming that the nuclei possess a spin, in which case transitions between symmetrical or between antisymmetrical states will have their usual intensity but transitions between symmetrical and antisymmetrical states will be very weak, of the order of the coupling of the nuclear spins. He then writes the following expression for the rotational specific heat,

$$\frac{C_r}{R} = \sigma^2 \frac{d^2}{d\sigma^2} \log Q,$$

$$Q = \beta[1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \ldots] + 3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \ldots, \quad (1)$$

where $\sigma = h^2/8\pi^2 IkT$ and β is the ratio of the weights of the symmetrical group of states to the antisymmetrical group. Hund has found that he obtains a close agreement between (1) and the observed specific heat curve only when β has about the value 2, that is when the symmetrical states have twice the weight of the antisymmetrical. He further obtains for this case $I = 1.54 \times 10^{-41}$ *gm.·cm.*^{2}, the moment of inertia of the H_2 molecule.

These values for β and I are not in agreement with the observed features of the band spectra of H_2. A careful analysis of the far ultra-violet bands of H_2 has been made by T.Hori† to whom I am greatly indebted for allowing me to see the manuscript of his work. Hori finds that the moment of inertia in the normal state has the value $I = 4.67 \times 10^{-41}$, and that the transitions between antisymmetrical terms are about three times as strong as the corresponding transitions between symmetrical terms, that is $\beta \approx \frac{1}{3}$. He does not find any

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*F.Hund, 'Z. f. Physik', vol. 42, p. 93 (1927).

†T.Hori, 'Z. f. Physik' *(in print)*.

lines corresponding to transitions between symmetrical and antisymmetrical terms. These values for β and I when set into (1) lead to a specific heat curve having a sharp and high maximum, in no way agreeing with the observed curve.

It now suggests itself that the difficulties encountered in comparing these sets of data may lie in the assumption that the symmetrical and antisymmetrical terms can combine, an assumption which determined the form of (1). The coupling of the nuclear spins with the spin of the molecule, which determines these transitions, will indeed be very small, much smaller than the coupling forces between the electronic spins and the orbits which give rise to the very week transitions between ortho- and para-helium. Let us make the assumption that the time of transition between a state symmetrical in the rotation, and an antisymmetrical state is very long compared with the time in which the observations of the specific heat are made. In this case we have in effect two distinct gases, the one formed from the symmetrical states with a specific heat C_s and the other containing the antisymmetrical states with a specific heat C_a, where

$$\left.\begin{aligned} \tfrac{C_s}{R} &= \sigma^2 \tfrac{d^2}{d\sigma^2} \log Q_s, \qquad Q_s = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \dots \\ \tfrac{C_a}{R} &= \sigma^2 \tfrac{d^2}{d\sigma^2} \log Q_a, \qquad Q_a = 3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \dots \end{aligned}\right\} \tag{2}$$

The final rotational specific heat of the mixture is

$$\frac{C_r}{R} = \frac{\rho C_s + C_a}{(1+\rho)R}, \tag{3}$$

where ρ is the proportion of symmetrical to antisymmetrical molecules. In Table I there is given a series of values of C_s/R and C_a/R computed for the argument σ.

It is evident that since C_s/R rises to a maximum of about 1.5 and C_a/R rises steadily to unity that ρ must have a value less than 1 if the curve C_r/R is to fit the experimental curve. The following method was used to determine ρ. The observed values for the specific heat of H_2 as given by Eucken[*], Scheel and Heuse[†], Giacomini[‡], Brinkworth[§] and Partington and Howe[¶] were plotted against the temperature. An averaging curve was drawn through

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[*] A.Eucken. 'Preuss. Akad. d. Wiss.', p. 141 (1912).

[†] K.Scheel and H.Heuse, 'Ann. d. Phys.', vol. 10, p. 173 (1913).

[‡] F.A.Giacomini, 'Phil. Mag.', vol. 50, p. 146 (1925).

[§] J.H.Brinkworth, 'Roy. Soc. Proc.', A, vol. 107, p. 510 (1925).

[¶] J.R.Partington and A.B.Howe, 'Roy. Soc. Proc.', A, vol. 109, p. 286 (1925).

Table I.

σ	$\frac{C_s}{R}$	$\frac{C_a}{R}$	$\frac{\frac{1}{3}C_s+C_a}{\frac{4}{3}R}$	$T_{\text{exp.}}$	$\sigma T_{\text{exp.}}$	$T_{\text{calc.}}$
1.2	0.193	0.0021	0.050	70	84.0	71.2
1.0	0.436	0.0106	0.117	85	85.0	85.5
0.8	0.875	0.0501	0.256	104	83.2	106.9
0.7	1.142	0.1038	0.363	118	82.6	122
0.6	1.374	0.206	0.198	140	84.0	142
0.5	1.464	0.381	0.652	176	88.0	171
0.4	1.341	0.635	0.811	223	89.2	214
0.35	1.224	0.767	0.881	251	87.9	244
0.3	1.111	0.886	0.942	286	85.8	285

these points and this curve was assumed to give the observed variation of the specific heat with temperature. A value of ρ was selected and C_r/R computed from (3) and for every point the value of $T_{\text{exp.}}$ was read off the observed curve. A column $\sigma T_{\text{exp.}}$ was then constructed which should consist of constant values if the computed curve agreed exactly with the observed curve. It was found that the best agreement occurred when $\rho = \frac{1}{3}$ that is when the antisymmetrical molecules are three times as numerous as the symmetrical ones. The values for C_r/R for this case are given in the fourth column of the table, followed by a column for $T_{\text{exp.}}$ and for $\sigma T_{\text{exp.}}$ (Although it is not possible to fix the value of ρ exactly from the present data, it can be shown that $\rho = \frac{1}{3}$ fits the observed curve distinctly better than $\rho = \frac{1}{3.5}$ or $\rho = \frac{1}{2.7}$).

Taken the average of $\sigma T_{\text{exp.}}$ to be 85.5, we may find the computed values for the temperature as given in the seventh column of the table. The agreement between $T_{\text{calc.}}$ and $T_{\text{exp.}}$ is very satisfactory, the greatest deviation (less than 4 per cent.) is within the limit of the experimental error. If $\sigma T = 85.5$ we find the moment of inertia of the hydrogen molecule to be $I = 4.64 \times 10^{-41}$ $gm.\cdot cm.^2$, in substantial agreement with the moment of inertia found by Hori from band spectra data.

In conclusion we may say that by assuming that the symmetrical and antisymmetrical rotational states of the hydrogen molecule do not combine during a time long compared with the time of the experiment, we obtain a specific heat curve which follows the observed curve to within the errors of observation, and that moreover the constants ρ and I are in good agreement with the values of these constants as found in the band spectrum of H_2.

[*Added June 16, 1927.* — It may be pointed out that the ratio of 3 to 1 of the antisymmetrical and symmetrical modifications of hydrogen, as regards the rotation of the molecule, is just what is to be expected from a consideration of the equilibrium at ordinary temperatures if the nuclear spin is taken equal to that of the electron, and only the complete antisymmetrical solution of the Schrödinger wave equation allowed.[*]

While it would not appear possible to produce only the one modification of the molecule by a combination of two hydrogen atoms since the heat of dissociation of H_2 is so much higher than the difference between the first rotational states, other experiments might be performed which would show the non-combining character of these two sets of rotational states and possibly even allow them to be separated. Indeed, the far ultra-violet absorption spectrum of H_2 at low temperatures would show at once whether the molecules all go into the zero state of rotation or whether they remain in the zero and first rotational states in the ratio of 1 to 3 as is suggested in the present note.]

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[*] W.Heisenberg, 'Z. f. Physik', vol. 41, p. 239 (1927), in particular see p. 264.